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Cesium Pentazolate: a New Nitrogen-rich Energetic Material

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Abstract. We report theoretical and experimental evidence for a new class of high-nitrogen content energetic material compounds consisting of molecular pentazoles, which are stabilized in the crystal phase upon introduction of elemental cesium. First-principles structural predictions show that the material with composition CsN_5 is thermodynamically stable above 15 GPa. Indexing of the measured X-ray diffraction spectra indicate the synthesis of this material at 60 GPa as well its stability upon decompression down to 24 GPa.

INTRODUCTION

In its triple bonded state, nitrogen gas (N_2) is one of the most abundant molecules on earth making up roughly 70 % of the atmosphere. In contrast, single and double bonded forms of nitrogen are rare. Any reaction involving the transformation from single or double N-N bonds to triple-bonded N_2 would release a large amount of stored chemical energy, thus making single and double bonded forms of nitrogen excellent components in high energy density materials (HEDMs) [1, 2, 3]. It is therefore of fundamental and practical interest to search for novel forms of nitrogen.

By introducing metallic impurities into the nitrogen matrix, electrons may be transferred from metallic to nitrogen atoms. This electron transfer can help stabilize novel forms of nitrogen, e.g. an ionic salt $\text{N}_5^+\text{AsF}_6^-$ [4]. Furthermore, by compressing high-nitrogen precursor materials to high pressures, the nitrogen atoms may interact with one another to form novel molecular clusters. Among such compounds, various azides (ammonium and alkali metal azides) are a promising family mainly due to the existence of the $\text{N}=\text{N}$ double bonds in the N_3 linear anion. There have been several previous theoretical and experimental studies that show novel forms of nitrogen may potentially be synthesized using azides (AN_3) as a starting material [5, 6, 7, 8, 9, 10, 11, 12].

Previous theoretical studies on alkali metal azides under constant relative stoichiometry (1:3) of the elements (A-N) indicate N_6 rings and infinite N chains become preferred at high pressures. However composition is an important parameter that has not been attempted to vary in previous searches for stable compounds at extreme pressures.

In this work we present results of a combined theoretical and experimental study of the Cs_xN_y system with variable stoichiometry. Our principal experimental diagnostics are x-ray diffraction. Crystal structure search for new Cs_xN_y compounds is performed at several pressures using the first principles evolutionary structure prediction method USPEX [13, 14, 15]. By comparing experimental and theoretical results we unambiguously confirmed synthesis of new compound with composition CsN_5 at 60 GPa as well its stability upon decompression down to 24 GPa.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

Crystal structure search for new Cs_xN_y compounds at 0.5 GPa, 30 GPa, and 60 GPa are performed by using the first principles evolutionary structure prediction method USPEX [13, 14, 15]. After the convex hull is calculated, additional crystal structure searches are performed at fixed stoichiometry and fixed molecular motifs with up to 6 formula units

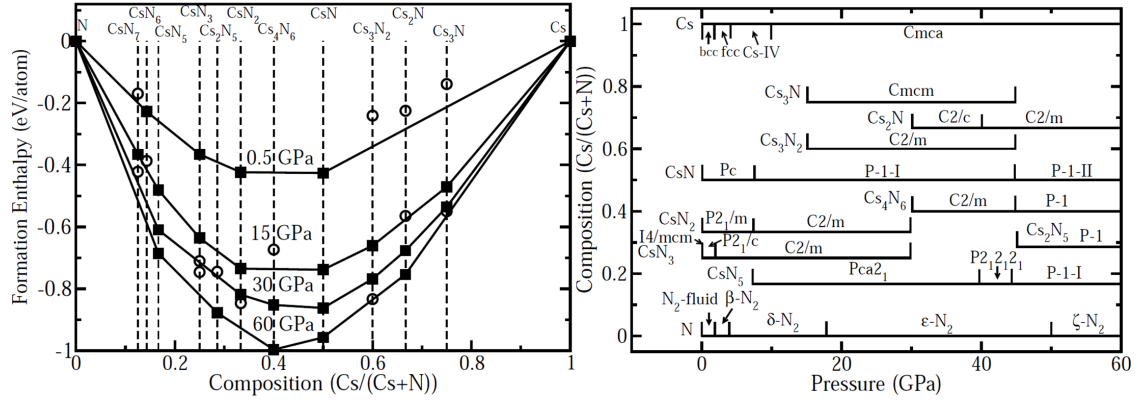


FIGURE 1. (a) Convex hull diagram at pressures 0.5 GPa, 15 GPa, 30 GPa, and 60 GPa. Solid squares represent stable phases, open circles – metastable phases. (b) Pressure-composition phase diagram of new Cs-N crystal phases discovered in simulations.

per unit cell. This method is used to efficiently search over a substantially large portion of the energy landscape. First-principles calculations are performed using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional within density functional theory (DFT) as implemented in VASP code [16]. Projector augmented wave (PAW) pseudopotentials and plane wave basis sets are used with an energy cutoff of 600 eV and a 0.05 \AA^{-1} k-point sampling. The dispersive correction by Grimme [17] is added on to take into account the long-range van-der Waals forces, which are significant due to the large polarizability of Cs.

Commercially available (Sigma-Aldrich) 99.99% pure CsN_3 is placed inside an argon gas purged glovebox and ground to fine powder. The sample fine powder including pressure sensors are loaded into diamond-anvil cell (DAC) sample chambers. The DACs cavities are filled cryogenically with either N or Ar and the pressure increased to the target pressure. Pressure is determined using known ambient temperature EOS of gold [18] and also calibrated ruby luminescence [19]. MAR355 CCD detector are used to collect pressure dependence X-ray diffraction (XRD) data at the Advanced Photon Source GSECARS (sector 13, $\lambda=0.3344 \text{ \AA}$) and at the Advanced Light Source Beamline 12.2.2 ($\lambda=0.4959 \text{ \AA}$). Although CsN_3 is transparent at ambient pressure, band closure upon increase of pressure results in an opaque sample above 30 GPa which allows an efficient heating of the sample by IR laser.

RESULTS AND DISCUSSION

The structural predictions reveal several new and interesting crystal structures with novel stoichiometries. The calculated convex hull is given in Figure 1(a) which represents the stable structures and stoichiometries [20], and the pressure stability range of each structure revealed in the simulations is given in Figure 1(b). The predicted crystal structures consist of several different types of nitrogen anions; atomic nitrogen, diatomic nitrogen, azides, N_4 chains, pentazoles, and N_6 hexagons.

One of the most interesting predicted structures consist of pentazole anions (N_5^-) and cesium cations with stoichiometry CsN_5 , shown in Figures 2(a-f). As seen in Figure 1(a), CsN_5 is on the convex hull above 15 GPa. In order to predict the lowest enthalpy polymorph of cesium pentazolate (CsN_5), structural searches are performed using the USPEX method at 30 GPa and 60 GPa. A rich variety of energetically competitive cesium pentazolate polymorphs are found and displayed in Figure 2(a-f). These structures differ by the orientation of the pentazoles with respect to one another and the arrangement of Cs atoms. The enthalpy of each of these phases relative to the ambient pressure phase, Pca2_1 , as a function of pressure is given in Figure 2(g). The lowest enthalpy polymorph between 50-80 GPa has P-1 symmetry (P-1-I), shown in Figure 2(d). The third highest enthalpy structure, which is still very close in enthalpy to the lowest enthalpy structure (P-1-I) at 60 GPa has space group Pnma , see Figure 2(f) for the snapshot of this structure at 60 GPa.

The relative enthalpy of cesium pentazolate ($\text{Pca2}_1\text{-CsN}_5$) compared to cesium azide with excess nitrogen ($\text{C2/m-CsN}_3 + \epsilon\text{-N}_2$) is also displayed in Figure 2(g) as a function of pressure that indicates $\text{Pca2}_1\text{-CsN}_5$ is lower in enthalpy, hence stable above just 7.1 GPa. These two phases of CsN_3 and pure nitrogen are chosen because they represent the

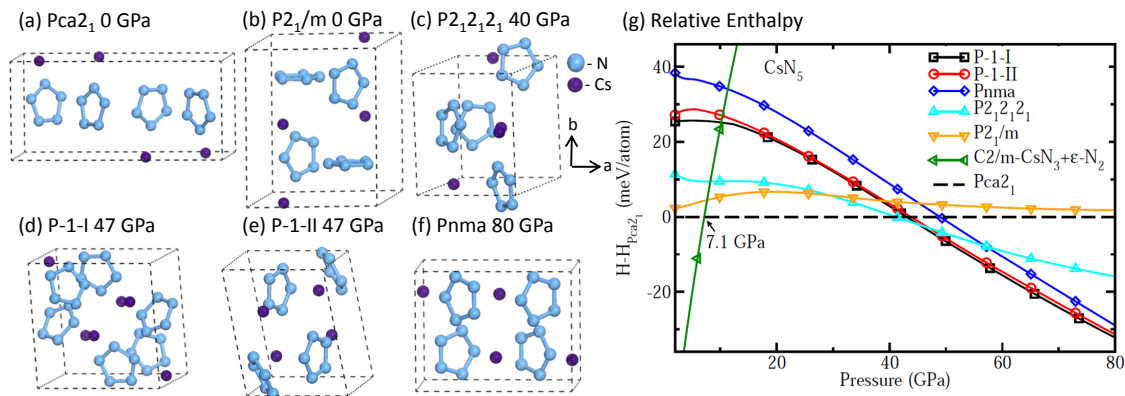


FIGURE 2. Snapshots (a-f) and relative enthalpy (g) of several cesium pentazolate (CsN₅) polymorphs discovered during the structure search. Structures (a,b) are the lowest energy structures at 0 GPa while structures (c-f) are energetically competitive at high pressures.

high pressure phases of CsN₃ and N that have been fully structurally characterized. It is remarkable that the pentazole anion can be stabilized at such a small pressure.

In order to synthesize the newly predicted cesium pentazolate (CsN₅) structure, cesium azide (CsN₃) is loaded into a DAC in the presence of excess N₂ and compressed to high pressures then laser heated. The XRD is measured to monitor the resulting structural and chemical changes that occur. Laser-heating of the CsN₃-N₂ mixture at ca 60 GPa results in an apparent drastic change of the XRD pattern of the quenched compound in the close vicinity of the laser heated spot. Remarkably, visual observation of the DAC indicates the presence of a transparent material exactly at the laser heated spot as shown in the inset to Figure 3(a). XRD patterns given in Figure 3(a) reveal the appearance of new intense narrow Bragg peaks with a simultaneous disappearance of the broad CsN₃ peaks.

The XRD pattern of the predicted Pnma-CsN₅ structure shows the best agreement with the measured XRD pattern quenched after laser heating as shown in Figure 3(a). There is also some overlap between the experimental spectra and other theoretically predicted CsN₅ polymorphs with lower symmetry. One of the peaks that stands out is the low-angle diffraction peak near 2.3° which also appears in the low-symmetry predicted structures P-1-I and P-1-II. Higher symmetry cesium pentazolate structures produce a diffraction peak near this angle. However, the intensity of this peak is zero for the perfect structure without defects or symmetry breaking probably due to some degree of non-hydrostatic loading. In addition, there are several other overlapping peaks between experiment and theoretical polymorphs of cesium pentazolate, such as the peaks near 4.7°, 6.2°, and 8° at 65 GPa. These peaks agree particularly well in the high-symmetry orthorhombic Pnma-CsN₅ structure as shown in Figure 3(a). The Bragg peaks of the new phase can be well indexed using a structure with space group Pxxx, such as the predicted Pnma structure.

Upon decrease of pressure the newly synthesized transparent phase is present down to 18 GPa as evidenced from XRD measurements and optical observations. The pressure-volume equation of state (EOS) based on the indexing compared to various scenarios are shown in Figure 3(b). The experimental EOS matches well the calculated EOS of cesium pentazolates with symmetries P-1-I and Pca2₁ for the full range of pressures studied. The measured EOS is also compared to those of theoretically predicted structures Cs₄N₆ and Cs₂N₅ which are composed of N₆ hexagons and N₅ rings respectively. However, as can be seen in Figure 3(b), the volume of these structures is significantly higher than that measured in experiment. The transparency of material in the laser heated spot, indicating a wide band gap material, is also in favor of the synthesis of the CsN₅ compound given that all other predicted stable stoichiometries (including metastable CsN₃ [8]) at the same pressure are calculated to be metallic or have small band gap. According to the calculated band structure of the P-1-I phase of CsN₅, cesium pentazolate is an insulator with a band gap of 3.2 eV at 60 GPa.

CONCLUSIONS

In summary, several new and interesting crystal structures have been predicted using crystal structure prediction methods that vary the composition of elemental cesium and nitrogen (Cs_xN_y). The most interesting crystal structures

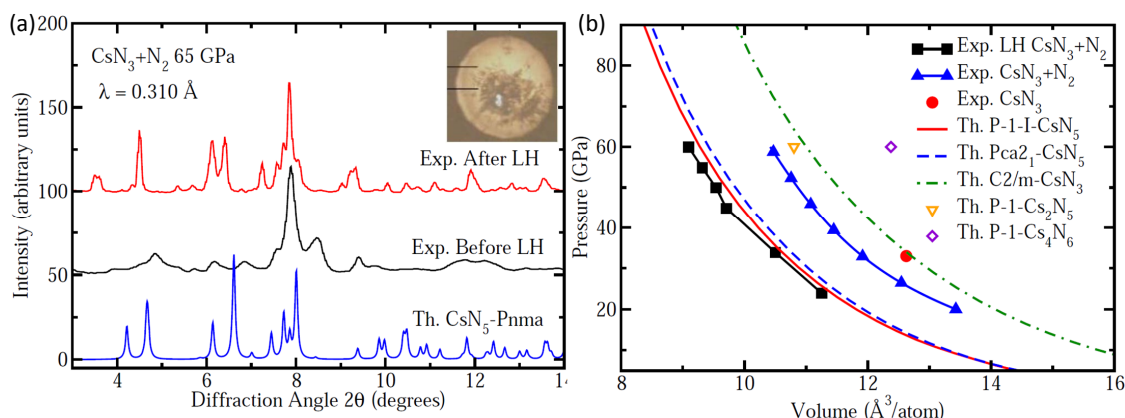


FIGURE 3. XRD patterns (a) and indexed pressure-volume equation of state (b) of the CsN_3+N_2 mixture before and after LH compared to theoretical structures. The inset in (a) shows a microphotograph of the sample after heating in transmitted light, indicating the transparency of the synthesized phase.

contain either N_4 chains, N_5 pentazoles, or N_6 rings. The presence of the alkali metal enhances the stability of these nitrogen molecular complexes to make them stable at high pressures. Newly predicted cesium pentazolate (CsN_5) is calculated to be lower in energy than CsN_3+N_2 above a pressure of just 7.1 GPa. The experimental validation for the predictions are performed by the successful synthesis of cesium pentazolate (CsN_5) near 60 GPa after laser heating of CsN_3 in a nitrogen-rich environment. The measured XRD spectra is in agreement with theory.

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